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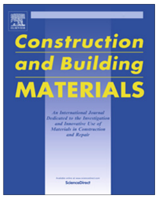

Recycling of limestone fines using $Ca(OH)_2$- and $Ba(OH)_2$-activated slag systems for eco-friendly concrete brick production

Woo Sung Yum, Yeonung Jeong, Heamin Song, Jae Eun Oh *

School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Ulju-gun, Ulsan 44919, Republic of Korea

HIGHLIGHTS

- Limestone fines (LF) was studied as a supplementary material in activated slags.
- Main activators for slag were $Ca(OH)_2$ or $Ba(OH)_2$.
- At early ages, the use of LF significantly improved strength in both activations.
- The use of LF significantly changed reaction products of $Ba(OH)_2$ activation.
- However, the use LF did not alter reaction products of $Ca(OH)_2$ activation.

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ABSTRACT

This study explored the possibility of using limestone fines (LF) as a supplementary material in activated slag binder systems using two types of activators (i.e., 10 wt% of $Ca(OH)_2$ or 10 wt% of $Ba(OH)_2$) and investigated the interactions of the activators with LF in each binder system through strength testing, powder X-ray diffraction, thermogravimetry, and mercury intrusion porosimetry. Using these binders, concrete brick samples containing LF were also made and examined for possible industrial applications. Although the influences of the LF addition on the strength, dissolution degree of the slag, reaction products, and pore-size distribution depended on the type and dosage of the activator, the addition was generally advantageous for all these aspects in both types of activations. The concrete brick made of 20 wt% LF using the $Ba(OH)_2$ activation fulfilled the Korean standard requirements of strength and water absorption for concrete bricks, and it also satisfied the criteria of the leaching test for possible toxic elements.

1. Introduction

Limestone is a main ingredient of Portland cement (PC) production. To manufacture PC, a mixture of about 1/3 clay and 2/3 limestone, by weight, is needed in raw materials [1]. Given that about 51 million tons of PC are annually produced in South Korea [2], a considerable amount of limestone is needed for manufacturing PC. The quarrying process for limestone generates a considerable volume of limestone dust, which is generally washed with water, resulting in a waste sludge called limestone fines (LF).

Limestone itself also has been widely used as an additive in various cementitious systems, such as PC [3,4], PC with supplementary cementitious materials [5–8], calcium sulfoaluminate cement [9–12], and alkali-activated materials [13,14]. Generally, it has been regarded as an inert filler due to its low reactivity [15]; however, it may accelerate cement hydration by supplying nucleation sites for the formation of hydration products and improve particle packing of cementitious systems [5,16]. In addition, the filler effect of limestone has been found to be superior to that of other minerals (usually quartz filler) [9,16], partially due to its interfacial properties and its additional ability to take part in ion-exchange reactions [16].

Earlier studies [15,17] reported the chemical reactions of limestone additive in PC hydration and its beneficial effect on strength development; for instance, the limestone additive modified cementitious phases (e.g., Al_2O_3-Fe_2O_3-mono (AFm)) in cement hydration from monosulfoaluminate ($Ca_4Al_2(SO_4)(OH)_{12}{\cdot}6H_2O$) to hemicarboaluminate ($Ca_4Al_2(CO_3)_{0.5}(OH)_{13}{\cdot}5.5H_2O$) and/or monocarboaluminate ($Ca_4Al_2(CO_3)(OH)_{12}{\cdot}5H_2O$) phases with additional formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$). These reactions simultaneously increased the total volume of solid phases and improved strength. LF probably would have similar physical and chemical properties as those of the limestone additives;

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* Corresponding author.
E-mail address: ohjaeeun@unist.ac.kr (J.E. Oh).

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however, although there were a few attempts to use it as a cement paste replacement, or fine aggregate, it is still rarely used in cementitious systems [18,19].

Unlike limestone, the use of LF as an additive material for PC is not regarded as suitable in construction because LF generally possesses high contents of moisture and mineral impurities, as it is an industrial waste by-product. Due to the same issues, LF is also difficult to recycle in most other industrial sectors. Thus, LF is mostly landfilled and an environmental hazard [20].

Many earlier studies tried to develop cementless binders using industrial by-products, such as ground granulated blast-furnace slag (GGBFS) or coal fly ash [21–24], to reduce the use of PC because the manufacturing process of PC produces a vast volume of CO_2, which is a greenhouse gas. Recent studies [25,26] have reported that the use of cementless binders could be a potential way to utilize slurry forms of industrial waste by-products (e.g., stone powder sludge or red mud) on a large scale as supplementary materials in producing construction products (e.g., concrete brick).

Thus, this study explored the possibility of using LF as a supplementary material in a GGBFS-based cementless binder system. As binder properties of cementless binder generally depend on the type of chemical activator [27–30], this study explored two different types of activators (i.e., calcium hydroxide ($Ca(OH)_2$) and barium hydroxide ($Ba(OH)_2$)) to investigate their influences on the effect of adding LF into the GGBFS-based cementless binder system. Properties of each activated GGBFS system were evaluated by means of compressive strength testing, powder X-ray diffraction (XRD), thermogravimetry (TG) with its differential (DTG) curves, and mercury intrusion porosimetry (MIP). Using these binders with LF, concrete brick samples were also made and tested for a possible industrial application.

2. Experimental procedures

Commercial GGBFS containing calcium sulfate was purchased. A sludge type of LF was obtained from the limestone mine quarry located at Sam-cheok in South Korea. To activate GGBFS, analytical grades of $Ca(OH)_2$ (Deajung Chemicals, Korea) and $Ba(OH)_2$ (Sigma Aldrich, USA) were used. To measure chemical compositions of the raw materials (i.e., GGBFS and LF), an X-ray fluorescence (XRF) (S8 Tiger wavelength dispersive WDXRF spectrometer, Bruker, Billerica, MA, USA) was used, and the results are shown in Table 1.

Particle size distributions of the raw materials were measured using a laser diffraction particle-size analyzer (HELOS (HI199) and RODOS, Sympatec, Clausthal-Zellerfeld, Germany) (see Fig. 1). The median particle sizes of GGBFS and LF were measured to be about 20 µm and 15 µm, respectively.

Fig. 2 shows the XRD patterns of the raw materials, which were obtained using a high-power X-ray diffractometer (D/Max2500V/PC, Rigaku, Japan) with Cu-kα radiation (λ = 1.5418 Å). Akermanite ($Ca_2Mg(Si_2O_7)$) and calcium sulfate anhydrite crystalline phases were identified in GGBFS; and calcite, quartz, mica ($H_2Fe_{0.47}O_{12}Rb_{0.99}Si_{2.96}$), dolomite ($C_2Ca_1Mg_1O_6$), and clinochlore ($Mg_{4.5}Fe_{0.5}Al_{1.84}Si_{3.16}O_{18}$) were identified in LF. The most obvious difference between GGBFS and LF was the presence of an amorphous phase in GGBFS. Due to the existence of an amorphous phase, GGBFS, unlike LF, showed an amorphous hump at ∼24°–35° in the XRD result (Fig. 2).

Table 1
Chemical compositions of raw materials by XRF.

Oxide	GGBFS (wt%)	LF (wt%)
CaO	46.38	63.00
SiO_2	32.54	19.60
Al_2O_3	12.82	8.10
MgO	3.54	2.80
SO_3	2.27	0.10
TiO_2	0.68	0.50
K_2O	0.40	2.30
Na_2O	0.31	0.00
$Fe_2$03	0.54	2.90
MnO	0.24	0.00
P_2O_5	0.00	0.20
Other	0.00	0.5

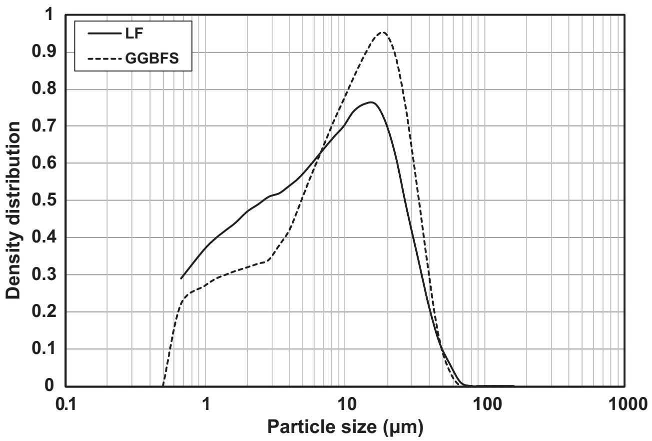

Fig. 1. Particle distributions of raw materials (note: the density distribution is dimensionless as it indicates the fraction of number of particles having a certain value of particle size).

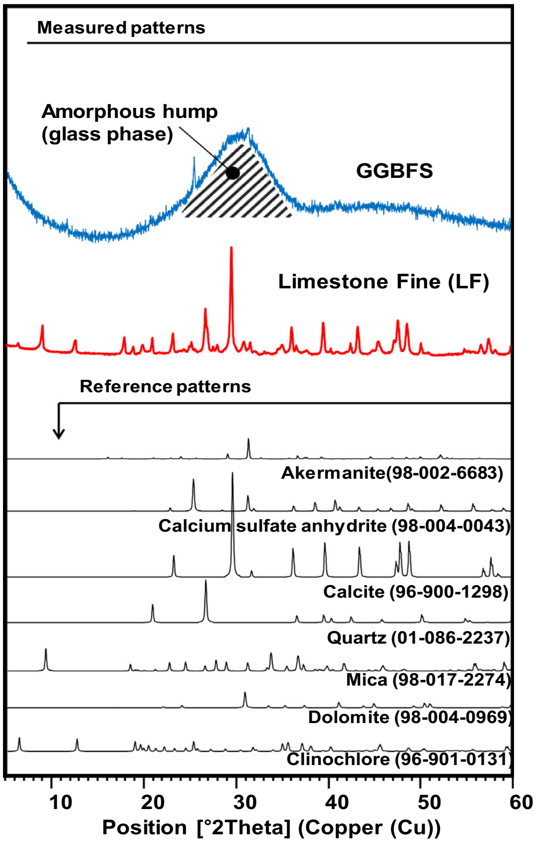

Fig. 2. XRD patterns of raw materials: GGBFS and LF.

The weights of crystalline phases were calculated semi-quantitatively by the normalized reference intensity ratio (RIR) method using the PANalytical X'pert HighScore Plus Program.